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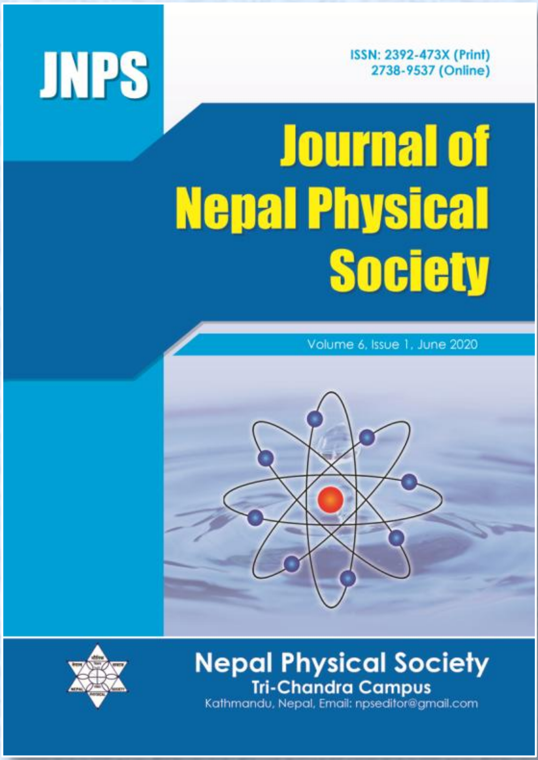

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Raman Spectroscopic Study of Valuable Idols from UNESCO World Heritage Sites in Kathmandu, Nepal

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Abstract

As an important step towards the conservation of valuable world heritage assets in Kathmandu, we performed Raman spectral studies on several valuable idols located in UNESCO World Heritage Sites for internal identification purposes. A spectrum of a stone idol in the Mohankali Chowk has a major band at 1093.5 cm^{-1} which may be identified as a C-O stretching vibration within the carbonate groups of $CaCO_3$. The Raman spectra of a bull situated in the same Chowk has two major bands at the wavenumbers of 1812.7 and 3552.4 cm^{-1}which are assigned as combined vibrational modes of CO_3 and hydroxyl stretching band, respectively. Similarly, the spectrum of a Shivalinga located at Pashupati Bankali has a major band at 467.7 cm^{-1}. This band is formed by the movement of the oxygen atom in Si-O-Si, which is a symmetric stretching mode indicating the presence of crystalline silica (SiO_2) in the Shivalinga. The Raman spectrum of Lord Changunarayan in Garuda located in the Changunarayan temple premises has a strong band at the wavenumber 462.6 cm^{-1}, denoting the presence of quartz (SiO_2).

Keywords: Heritage sites, Nondestructive, Raman spectrum, Sculpture.

1. INTRODUCTION

Sufficient research has not been carried out about the materials used in ancient art work and sculptures in Nepalese heritage sites. Publications on the techniques and materials used by ancient Nepalese artists are few and far in-between. Although a few researchers have conducted to study these topics, there are no papers focused specifically on the heritage sites of Nepal. For example, S. Fitzgerald investigated an ancient Nepalese manuscript containing a color illustration of Amida, a celestial Buddha described in the Mahāyāna school of Buddhism using the technique of micro x-ray fluorescence (micro XRF). The sample for his study was provided by the Classical Manuscripts Digital Archive Study Center (Ryukoku University Library, Japan). The colors, elements and assignment of pigments identified for different points of the manuscript are tabulated [1]. Similarly, Mazzeo et al. have worked on the mural painting pigments from the Thubchen Lakhang monastery located in Lo Manthang, upper Mustang, Nepal. It was built with rammed mud and wood by order of the King in 1470, completed by 1472, and renovated several times afterwards. The first results of scientific examination aimed at characterizing the composition of the pigments present in paint samples collected from the south and east wall decorations is presented [2].

The aim of this work is to perform a spectroscopic study of cultural heritages within UNESCO World Heritage Sites in Kathmandu, Nepal. Since theft and counterfeit pose great threats in the case of sculptures, the conservation of these invaluable properties for our future generations is an important task of this time. Most of the cultural centers of Nepal are concentrated within Kathmandu valley. Among them, an important attraction is Hanuman Dhoka Durbar Square. This feature is important from both cultural as well as historical perspectives. For this reason, we have primarily selected this palace's premises for our study. In addition, we also have selected some important objects from other heritage sites, including Pashupati and Changunarayan temples.

In our study, we have applied Raman spectroscopy, which is a nondestructive technique that provides accurate recognition of objects under study without any damage and change. This is based on the inelastic scattering of monochromatic light, usually from a laser source. Photons of the incident laser light are absorbed by the sample and then reemitted. When the frequency of the reemitted photon is shifted up or down in comparison to the original frequency, this is called the Raman Effect. A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (usually in units of wave numbers, cm^{-1}). This shift provides information about vibrational, rotational and other low frequency transitions in molecules. The peaks in a Raman spectrum correspond to molecular vibrations specific to the sample being analyzed. These Raman peaks are an internal identification (finger prints) of the substance under study. Therefore, if the unique spectroscopic identification of such objects is recorded, this database can be of use when the need for verification arises at any later time.

However, because of the disastrous earthquake on April 25, 2015, many buildings containing the objects aimed for this study were either destroyed or were at risk and even researchers were not permitted to enter these locations. For the study of these objects, we had to wait until reconstruction work will be complete. Almost a year after the disaster, Hanuman Dhoka Durbar Museum Development Committee has made some arrangements in the destructed site and we have been permitted to work in some selected areas with extreme care. Similarly, in other heritage sites as well, we have chosen important idols accessible at this time for study.

2. EXPERIMENT

Here, we have used a fully portable *EnSpectr RaPort* instrument to carry out in-field spectroscopic examination. Raman spectroscopy provides fingerprint spectra of materials, including solids, liquids, powders, gems and gels, through a non-destructive and non-contact technique. It utilizes a 30 μm entrance slit, 1800 g/mm holographic grating, cutting-edge low pass filter, as well as a 30 mW single mode laser emitting at 532 nm to provide high accuracy Raman measurements in a broad spectral range from 90 to 4000 cm^{-1} [3]. This method has a wide range of applications in different types of art works, forensic sciences, environment protection, war against terrorism and chemical analysis [4, 5].

3. RESULTS AND DISCUSSION

Mohankali Chowk is the oldest courtyard within Hanuman Dhoka Durbar, Fig. 1(a). Its walls have been decorated by installing a number of wood carvings and stone/metal idols which are centuries old. Fig. 1(b) shows the spectrum taken from the back of a stone idol [Inset: Fig. 1(b)] located at the courtyard's front end. Measurements were performed on the existing conditions of the idols (without cleaning off the surface). The spectrum, after base line correction, shows a prominent peak at 1093.5 cm^{-1}. This peak is identified as the C-O stretching vibration within the carbonate groups of $CaCO_3$ [6-8]. There are a few other minor bands at 1857.9 and 719.2 cm^{-1}.

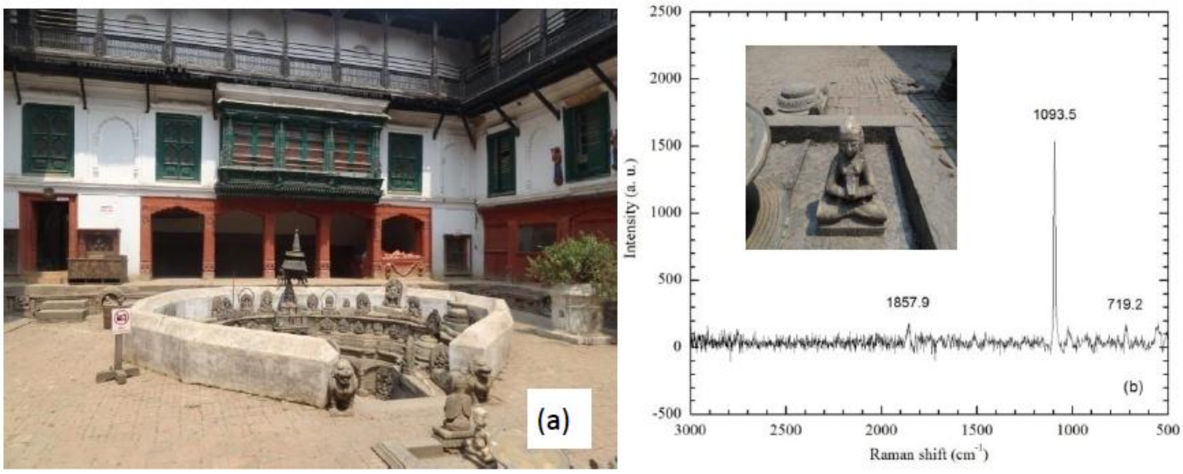

***Fig. 1**: (a) Mohankali Chowk within the Hanuman Dhoka Durbar Square, (b) Raman spectrum taken from the back of the stone idol (inset), installed in the Mohankali Chowk, using 532 nm laser and 2000 ms exposure time.*

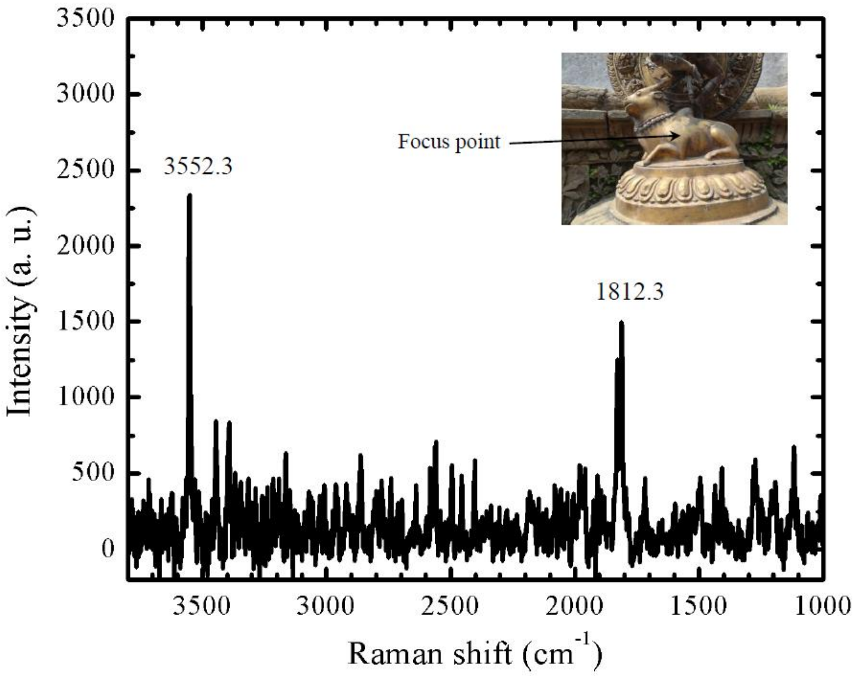

***Fig. 2**: Raman spectrum of a bull (inset) situated in the Mohankali Chowk within the Hanuman Dhoka Durbar Square measured by 532 nm laser and 200 ms exposure time.*

The mode at 1857.9 cm^{-1} is combination of the CO_3 vibrational modes [9]. The other band at 719 cm^{-1} is CO_3 bending mode [7]. Thus, the idol is likely to be made up of calcite. Fig. 2 shows the Raman spectrum of a bull (inset) situated in the Mohankali Chowk within the Hanuman Dhoka Durbar Square measured by 532 nm laser and 200 ms exposure time. There are two major peaks at the wavenumbers of 1812.3 and 3552.3cm^{-1}. These bands may be due to the formation of a layer of basic carbonate of copper (malachite) on the surface of the idol formed by corrosion of copper with atmospheric oxygen, carbon dioxide and water vapor.

The peak at 1812.7 cm^{-1} is a combination of different vibrational modes of CO_3 and the peak at 3552.4 cm^{-1} is a hydroxyl stretching band [9-11]. This indicates that copper is definitely the major content of this idol.

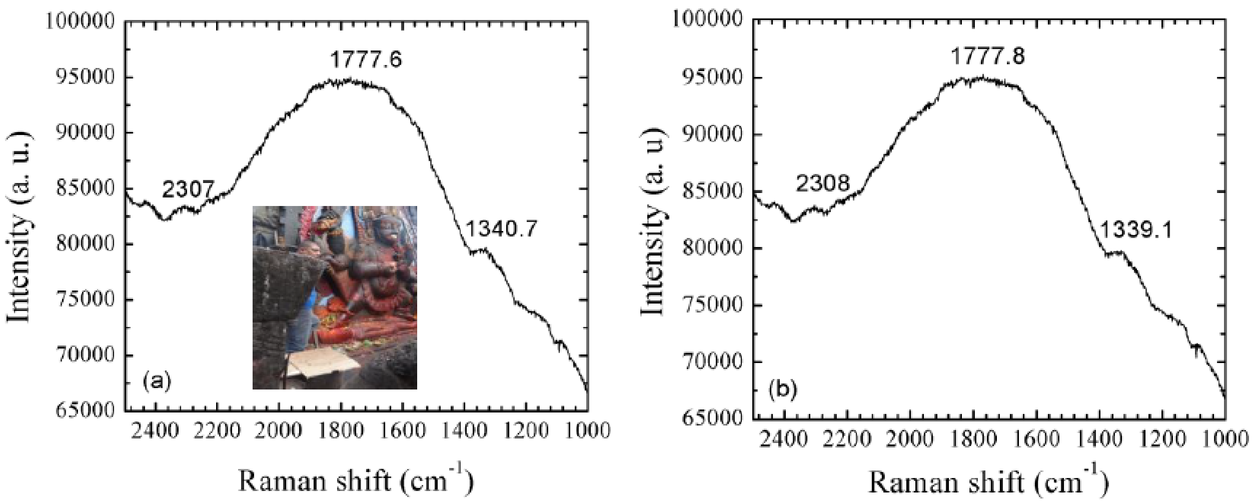

***Fig. 3**: Raman spectra of (a) left toe-tip, and (b) right toe-tip of Kaal Bhairav idol taken with 532 nm laser and 400 ms exposure time. Inset of Fig. 3(a) shows the Kaal Bhairab idol at Hanuman Dhoka Durbar Square.*

The Kaal Bhairav idol, situated in Hanuman Dhoka Durbar Square, [Inset: Fig. 3 (a)] is one of the largest stone idols in Kathmandu which symbolizes the terrifying aspects of the Hindu god Shiva. For spectrum collection, various spots on the idol relatively clean and free of materials offered by devotees have been selected. The spectra of the left and right toe of Kaal Bhairav are presented in Fig. 3(a) and 3(b). Similar spectra were observed in other chosen spots, including left and right thumbs (not shown), with a wide band at around 1778 cm^{-1}. Both spectra in the wave number range of 1000 - 2500 $cm^{-1}$are seen to overlap. This indicates that the material contained in the idol is homogenous. Besides this, several minor peaks are observed at about 860, 1030, 1320, 2812, 3238, 3502 and 3831 cm^{-1} (not shown). These peaks may be caused by different modes of vibrations of alcohol [12], which is offered to the Kaal Bhairav during worship as a part of the tradition.

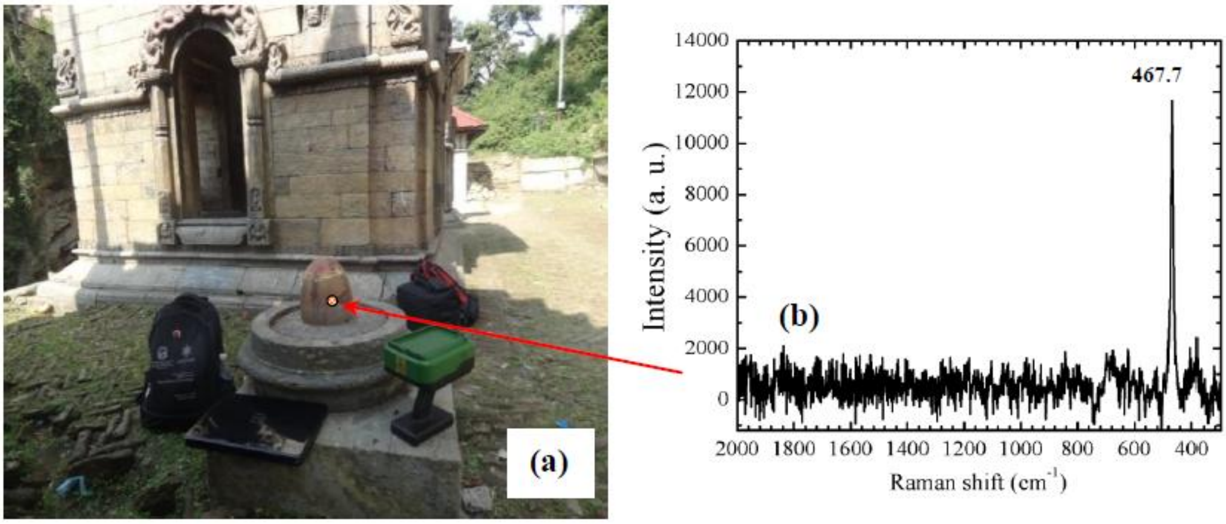

***Fig. 4**: (a) A Shivalinga between a series of small temples at Bankali within Pashupati temple premises (b) Raman spectrum at the marked circle of the Shivalinga taken by 532 nm laser, and 400 ms exposure time.*

Fig. 4 (a) shows a Shivalinga at the middle of a series of small temples (only one half of the line behind the idol is shown) at Bankali, within Pashupati temple premises, another world heritage site. Fig. 4 (b) shows a spectrum taken at the marked spot of the Shivalinga (pointed by an arrow). A strong narrow band is observed at the wave number 467.7 cm^{-1}. This band results from the movement of the oxygen atom in a Si-O-Si, a totally symmetric stretching mode. This band indicates the presence of crystalline silica (SiO_2) [13]. We observed similar bands at other spots of the Shivalinga. This indicates that the material used to construct Shivalinga is homogeneous.

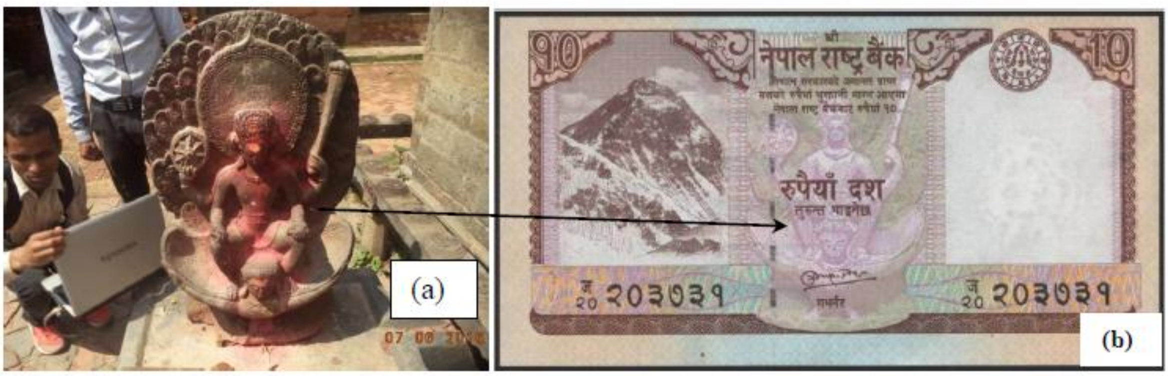

***Fig. 5**: (a) Image of Lord Changunarayan (a form of an appearance of Vishnu) riding Garuda located in the Changunarayan temple premises, (b) Image of the same Idol that appears in the Nepalese banknote of 10 rupees.*

Fig. 5 (a) shows the image of the Lord Changunarayan (an appearance of Hindu god Vishnu) in Garuda located in Changunarayan temple premises near Changunarayan village in Kathmandu valley, yet another UNESCO world heritage site. A Garuda is a mythical bird in both Hinduism and Buddhism, with the body of an eagle and head of a human. Garuda is the *Baahana* (vehicle) of the Lord Vishnu. This is considered as a very important idol and its image appears on the Nepalese 10 rupees banknote [Fig. 5 (b)].

Figure (6) shows the Raman spectrum, after baseline correction, taken from the back of the Vishnu idol shown in Fig. 5 (a). A strong peak is observed at the wave number 462.6 cm^{-1}. This is band of quartz (SiO_2) [14-17].

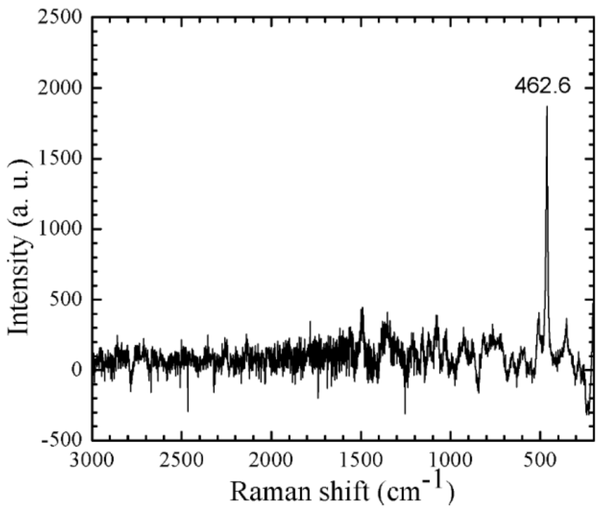

Fig. 6*: Raman spectrum from the back of Vishnu idol shown in figure 5(a) taken by 532 nm laser and 2000 ms exposure time.*

4. CONCLUSION

In this work, as an important step towards the conservation of the valuable world heritage assets in Kathmandu, we have applied Raman spectroscopy on various idols within a number of UNESCO world heritage sites in Kathmandu Valley. Thus, we are able to speculate the possible material composition of the objects by obtaining and analyzing the spectra. A spectrum taken from the back of a stone idol situated near the front end of the Mohankali Chowk in the Hanuman Dhoka Durbar Museum has a major band at 1093.5 cm^{-1}. This correlates with the C-O stretching vibration within the carbonate groups of $CaCO_3$. The Raman spectrum of a bull situated within the same Chowk has two major bands at the wave numbers 1812.7 and 3552.4 cm^{-1}. These bands have been identified as basic carbonates of copper, possibly formed on the idol surface by corrosion of copper with atmospheric oxygen, carbon dioxide and water vapor. The band at 1812.7 cm^{-1} reflects a combination of different vibrational modes of CO_3 and the other band at 3552.4 cm^{-1} is a hydroxyl stretching band. The Raman spectra of Kaal Bhairav idol located in the Hanuman Dhoka Durbar premises has a wide band at around 1778 cm^{-1} and several minor bands. A spectrum of a Shivalinga located at Bankali, Pashupati shows a strong narrow band at 467.7 cm^{-1} indicating the presence of crystalline silica (SiO_2). Spectra taken at other spots of the Shivalinga have similar peaks at about the same wave number, which indicates the homogeneity of the Shivalinga surface material. Raman spectrum of Lord Changunarayan has a strong band at the wave number 462.6 cm^{-1}, which has been assigned as a band of SiO_2 (quartz).

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